

(12) **UK Patent Application** (18) **GB** (11) **2 257 358** (13) **A**

(43) Date of A publication 13.01.1993

(21) Application No 9212430.4

(22) Date of filing 11.08.1992

(30) Priority data

(31) 4118306

(32) 12.08.1991

(33) DE

(71) Applicant

Whell Inter AG

(Incorporated in Switzerland)

Gartenstrasse 2, CH-6300 Zug, Switzerland

(72) Inventor

Walter Hefel

(74) Agent and/or Address for Service

Baron & Warren

18 South End, Kensington, London,

W8 5BU, United Kingdom

(51) INT CL^{*}

A61K 9/50

(52) UK CL (Edition L)

A5B BLL B829 B837

C3H HH1 H203 H221 H230

U1S S1081 S1091 S1092 S1814

(56) Documents cited

GB 1550153 A

GB 1440217 A

GB 1201014 A

GB 1072795 A

GB 0833458 A

GB 0788291 A

GB 0766889 A

GB 0708160 A

EP 0235988 A1

EP 0159602 A2

EP 0094513 A2

EP 0017115 A2

(58) Field of search

UK CL (Edition K) A5B BLL

INT CL^{*} A61K

Online databases: WPI

(54) Protected vital substances

(57) Organic raw materials, intermediates and end products for nutrition and for use for technical purposes are described which contain vital substances in the form of vitamins, enzymes, coenzymes, minerals, trace elements and/or microorganisms, the vital substances being embedded, separately with regard to function, in carrier substances with formation of protective films against harmful effects so that, with sufficient moisture absorption, in vivo and in vitro biocatalytic processes can be initiated and controlled. In particular, the products can be shaped by processing by a thermoplastic method to give utility and packaging articles, and the used utility forms can be disposed of by biocatalytic processes owing to the presence of active vital substances. The examples include the coating of enzymes with polysaccharides.

GB 2 257 358 A

- 1 -

**PROTECTED VITAL SUBSTANCES FOR INCORPORATION
INTO ORGANIC RAW MATERIALS, INTERMEDIATES AND
END PRODUCTS**

The invention relates to organic raw materials, intermediates and end products for nutrition and for use for technical purposes, which contain vital substances in the form of vitamins, enzymes, coenzymes, minerals, trace elements and/or microorganisms.

Raw materials, intermediates and end products obtained from vegetable and animal starting materials contain bacteria, microorganisms, vitamins, enzymes, coenzymes, minerals and trace elements. These vital substances are responsible for the functioning of biocatalytic processes.

The processing methods commonly used in industry aim at obtaining products which have as low a content of bacteria and microorganisms as possible, in order to be able to influence the shelf life of the product with as small amounts of added preservatives as possible. The washing, blanching, heating, compression, milling and granulating processes used eliminate not only bacteria, microorganisms and toxic compounds as well as inhibitors but destroy in particular the highly complicated proteins which play a decisive role predominantly in biocatalytic processes. Thus, it has not been possible to date in such processes to retain the vital substances in sufficiently active form for initiating biocatalytic processes.

Vital substances are becoming increasingly important for influencing biocatalytic processes. It is possible to initiate and control not only in vivo metabolic processes but also in vitro industrial processes. In the disposal of organic products for further use, these processes are of particular importance since they permit problem-free and controlled degradation.

It is the object of the invention to protect vital substances, such as vitamins, enzymes, coenzymes, microorganisms, minerals and trace elements separately with regard to function and to incorporate them in organic raw materials, intermediates and end products, the activity of the vital substances being retained after processing, shaping and use, even under heat and pressure shocks.

The invention relates to organic raw materials, intermediates and end products containing vital substances and intended for nutrition and for use for technical purposes, which are characterised in that the vital substances are embedded, separately with regard to function, in carrier substances with formation of protective films against harmful effects so that, with sufficient moisture absorption, in vivo and in vitro biocatalytic processes can be initiated and controlled. Suitable protective substances are preferably sodium salts and potassium salts of silicic acid and nonionic polysaccharides, in particular from the family consisting of the galactomannans.

Organic raw materials, intermediates and end products are of particular importance for nutrition and for use for technical purposes, in which the vital substances embedded, separately with regard to function, in carrier substances with formation of protective films are embedded in a component mixture which can be processed by a thermoplastic method and is of vegetable and/or animal origin and at least one component of which consists of a natural fibre which can be used for food.

The component mixtures according to the invention and containing vital substances protected separately with regard to function can be shaped into utility and

packaging articles by processing by a thermoplastic method.

The invention furthermore relates to protected vital substances for incorporation in organic raw materials, intermediates and end products for nutrition and for use for technical purposes, which are characterised in that vital substances in the form of vitamins, enzymes, coenzymes, minerals, trace elements and/or microorganisms are embedded, separately with regard to function, in carrier substances with the formation of protective films against harmful effects so that, with sufficient moisture absorption, in vivo and in vitro biocatalytic processes can be initiated and controlled.

Coenzymes contain electrolytes, minerals and trace elements with, for example, aluminium, iron, cobalt, copper, magnesium, manganese, phosphorus and zinc. Balanced mixtures tailored to the requirements are commercially available.

A few thousand enzymes are known, over 100 being available in crystalline form and some of these being synthesised.

The sensitivity of these highly complicated polypeptide complexes makes it appear appropriate to have available, quantitatively separate and qualitatively protected, holoenzymes, apoenzymes, coenzymes and the like for biocatalytic processes. The functions of six groups of enzymes should be noted: hydrolases, isomerases, ligases and lyases, oxidoreductases and transferases, some important enzymes being amylases, bromelins, chymotrypsin, enterokinase, erepsin, hyaluronidase, catalase, cathepsin, lipases, pancreatin, papain, pepsin, proteases and trypsin.

Both deficit enzyme contents in foods and animal feeds and prematurely initiated biocatalytic processes are known and can be counteracted, according to the invention, by formation of the protection of the various vital substances separately with regard to function.

According to the invention, vital substances, such as, for example, microorganisms, enzymes, coenzymes, electrolytes with minerals and trace elements, are therefore protected separately from one another by formation of protective layers and together initiate biocatalytic processes only on absorption of a certain amount of moisture.

Sodium salts and potassium salts of silicic acid are preferably suitable for protecting coenzymes while polysaccharides, in particular guar endosperm flour and carob endosperm flour, are particularly suitable for protecting polypeptide complexes as enzymes. The penetration of moisture can be effectively delayed by the protective film formed.

The vital substances to be protected are embedded in a protective film as a rule by mixing the vital substances with the protective substance with subsequent drying under mild conditions. The formation of the protective film can be carried out in the presence of water, for example in a fluidised bed.

By the addition of aqueous fat and/or oil emulsions with the use of unsaturated oils during the formation of the protective layer, the water repellancy of the protective film can be further increased.

The vital substances embedded according to the invention in carrier substances separately with regard

to function and with formation of protective films have a long shelf life, can be incorporated in organic raw materials, intermediates and end products for nutrition and for use for technical purposes and can be processed by conventional processing means, such as extruders and injection molding machines, into utility and packaging articles, such as, for example, into containers and packages for solid, pasty and liquid media, packaging materials and films which are edible, feedable and enzymatically and bacterially degradable and can be used as food and/or animal feed. The activity of the vital substances is retained and can be triggered in the desired manner after processing, in the presence of sufficient moisture. To avoid molecular changes in the mixtures with vital substances during the final processing to utility forms, care will of course also be taken to use gentle batchwise and continuous processing methods so that even ingredients which are effective from the point of view of nutritional physiology, such as, for example, proteins (amino acid), unsaturated fatty acids and the like, are not damaged.

Particularly preferred products of the invention consist of component mixtures which can be processed by a thermoplastic method and are of vegetable and/or animal origin and at least one component of which consists of a natural fibre which can be used for food, the vital substances in the form of vitamins, enzymes, coenzymes, minerals, trace elements and/or microorganisms, embedded separately with regard to function in carrier substances with formation of protective films, being incorporated in these mixtures. According to the invention, component mixtures consisting of seeds, cereals, vegetables, fruit, including ground fruits and tubers, and roughage thereof (nutrient fibres) and/or animal products,

optionally together with spices and additional components, are combined with the vital substances protected separately with regard to function. The mixture containing the protected vital substances can then be converted into plastifiable mixtures in intermediate process steps or in one step and can be shaped by known processing means into utility articles with retention of the activity of the vital substances.

According to the invention, vital substances, such as vitamins, enzymes, enzyme mixtures, microorganisms, coenzymes, minerals and trace elements, thus remain ready for functioning in separate and protected form in raw materials, intermediates and end products. With appropriate doses of the protected vital substances, it is possible to carry out controlled and distinctive biocatalytic processes.

In nutrition, medicine and disposal (further utilisation of used materials), protected and controlled action mechanisms for biocatalytic processes are becoming more and more important.

The particular properties of nonionic polysaccharides which enable them to enter into and form associations and hydrogen bridges with starches and celluloses make them particularly appropriate for use as protective colloids and emulsifiers. The extremely high rapid water-binding capacity blocks and delays the water absorption in association with the imperviousness of the particle sizes of the coenzyme and enzyme powders.

The Examples which follow serve to illustrate the invention.

Example 1

Coenzymes (metal salts, minerals and trace elements)

are dispersed in commercial form in sodium waterglass (sodium salt of silicic acid) and then dried by means of a drum dryer or spray dryer. The resulting coenzyme powder embedded in a protective film is sieved and is stored until required for further processing.

The coenzyme powder is friable and can therefore be readily incorporated into the mixtures. Immediately before final processing, the waterglass suspension can also be used without intermediate drying. Relatively small amounts of active substances are required in the coenzyme powder in the food and animal feed sector. The daily requirement is between 20 and 2000 mg. The silicic acid or its sodium or potassium salt in the form of waterglass can be laden with up to 90% of active substances.

The coenzymes, minerals and trace elements are embedded in self-crosslinking silicic acid and are effectively available only with appropriate moisture absorption accompanied by ion flow.

Example 2

In this Example, enzymes are embedded in a nonionic polysaccharide (guar endosperm flour).

Enzymes or enzyme mixtures are mixed into fine guar endosperm flour and sprayed in a fluidised bed with water at room temperature until a protective film has built up and paste formation has taken place. The particles with the colloidal protective film are dried in a warm air stream under mild conditions, and the exhaust air temperature should not exceed 60°C. The moisture content varies between 4 and 7%. The enzyme powder is sieved and is stored until required for further processing.

In the fluidised bed, the granulation can be influenced by the spraying rate and the choice of the spray nozzle. The enzyme powders are obtained in relatively narrow particle size ranges after drying. The particle sizes of the enzyme powders and the density are important in the case of final processing under high pressures.

Example 3

This Example shows that the enzymes or enzyme mixtures are embedded in a polysaccharide (carob endosperm flour) which is soluble only in hot water, and that formation of a protective film is effectively supported by spraying in an aqueous polysaccharide solution.

Enzymes or enzyme mixtures are mixed into fine carob endosperm flour and sprayed into a mixer together with a 1 to 2% carob endosperm flour solution in hot water until paste formation occurs. During drying under mild conditions, a colloidal protective film forms around the particles. The enzyme powder is sieved and is stored until required for further processing.

By using polysaccharides which are soluble at elevated temperatures, the barrier to moisture is increased and penetration of said barrier can be substantially delayed.

Example 4

In this Example, aqueous oil emulsions which influence the water repellancy are used.

Enzymes or enzyme mixtures are incorporated in oil and emulsified with a 1 to 2% aqueous guar endosperm flour solution in the emulsifier and sprayed into fine guar

flour with mixing until paste formation has taken place and a colloidal protective film forms on drying. The dry material is sieved and stored.

Example 5

This Example shows that the water repellancy is very pronounced when a polysaccharide which is soluble only in hot water is used together with oil emulsions.

Enriched microorganisms are incorporated in fine carob endosperm flour and sprayed with a 1 to 2% aqueous carob endosperm flour oil emulsion until wetting tends toward paste formation. The dry material is sieved and stored.

Example 6

Enzymes or enzyme mixtures are homogenised in guar endosperm flour in a mixer. 1.5 parts of water are added to one part of dry mixed material via a spray with a metering rate of 10 litres of water per second. The moist material is further mixed for not more than 5 minutes and then introduced into a fluidised-bed dryer via a granulator. The gentle drying is carried out in a warm air stream, the drying process being terminated after an exhaust air temperature of 60 to 62°C has been reached. The moisture content is about 4 to 6%. The dry material is sieved and stored.

Considerable compaction without application of pressure occurs as a result of the rapid addition of water. The particle size of the granules obtained can be adjusted by means of the various perforated sieve inserts. It is possible to produce fractions in narrow particle size ranges. The moisture absorption can be particularly easily controlled. Furthermore, highly

sensitive substances can be particularly readily embedded. Small amounts of active substances can be readily distributed and exactly metered. Loads up to 90% are possible.

Example 7

Soft wheat wholemeal flour is mixed in the mixer with the calculated amounts of coenzyme powder and enzyme powder protected by embedding in nonionic polysaccharides and is moistened with water until ball formation occurs on pressing with the ball of the thumb. As a rule, 50% of water are required. The desired shaping is carried out on a press or injection machine. The still moist mouldings are dried in an air stream at below 60°C.

This Example shows that coenzyme and enzyme powders embedded in nonionic polysaccharides can be processed on industrial apparatuses, such as, for example, presses, extruders or injection presses, to give crude products, intermediates or end products. Heat and pressure applications do not destroy the active substances embedded in the nonionic polysaccharides.

Example 8

The procedure was similar to that of Example 7, except that, instead of soft wheat wholemeal flour, other cereal flours are used in conjunction with proteins and nutrient fibres and combined with, for example, vegetable, fruit, meat and fish powder. The moisture content of the particular compositions must be adjusted before the final processing to utility forms. The utility forms can be adapted to receive various bodies.

CLAIMS:

1. Organic raw materials, intermediates and end products for nutrition and for use for technical purposes, which contain vital substances in the form of vitamins, enzymes, coenzymes, minerals, trace elements and/or microorganisms, characterised in that the vital substances are embedded, separately with regard to function, in carrier substances with the formation of protective films against harmful effects, so that, with sufficient moisture absorption, in vivo and in vitro biocatalytic processes can be initiated and controlled.
2. Organic raw materials, intermediates and end products according to Claim 1, characterised in that coenzymes which are embedded in crosslinked silicic acid are present.
3. Organic raw materials, intermediates and end products according to Claim 1, characterised in that enzymes which are embedded in nonionic polysaccharides with formation of a protective film are present.
4. Organic raw materials, intermediates and end products according to any of Claims 1 to 3, characterised in that microorganisms which are embedded in nonionic polysaccharides with formation of a protective film are present.
5. Organic raw materials, intermediates and end products according to Claim 3 or 4, characterised in that the vital substances are embedded in galactomannans which are soluble in cold and/or hot water.
6. Organic raw materials, intermediates and end products according to any of Claims 1 to 5,

characterised in that the vital substances are embedded in a fat-containing protective film.

7. Organic raw materials, intermediates and end products according to any of Claims 1 to 6, characterised in that the protected vital substances additionally contain fragrance materials, flavours, spices and/or colorants.

8. Organic raw materials, intermediates and end products according to any of Claims 1 to 7, characterised in that the vital substances embedded, separately with regard to function, in carrier substances with formation of protective films are incorporated in a component mixture which can be processed by a thermoplastic method and is of vegetable and/or animal origin and at least one component of which consists of a natural fibre which can be used for food.

9. Organic end products according to any of Claims 1 to 8, characterised in that they are shaped into utility and packaging articles by processing by a thermoplastic method.

10. Process for the preparation of organic intermediates and end products according to Claim 8 or 9, characterised in that the protected vital substances are added to the starting component mixture, wet with water and shaped into utility forms.

11. Process according to Claim 10, characterised in that, in order to protect the vital substances, the shaped articles remain moist and are dried by subsequent drying of the utility forms.

12. Protected vital substances for incorporation in

organic raw materials, intermediates and end products for nutrition and for use for technical purposes, characterised in that vital substances in the form of vitamins, enzymes, coenzymes, minerals, trace elements and/or microorganisms are embedded, separately with regard to function, in carrier substances with the formation of protective films against harmful effects so that, with sufficient moisture absorption, in vivo and in vitro biocatalytic processes can be initiated and controlled.

13. Protected vital substances according to Claim 12, characterised in that coenzymes are embedded in crosslinked silica.

14. Protected vital substances according to Claim 12, characterised in that enzymes are embedded in nonionic polysaccharides with formation of a protective film.

15. Protected vital substances according to Claim 12, characterised in that microorganisms are embedded in nonionic polysaccharides with formation of a protective film.

**Examiner's report to the Comptroller under
Section 17 (The Search Report)**

GB 9212430.4

Relevant Technical fields

(i) UK Cl (Edition K) A5B (BLL)

(ii) Int Cl (Edition 5) A61K

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Search Examiner

J F JENKINS

Date of Search

30 SEPTEMBER 1992

Documents considered relevant following a search in respect of claims 1 TO 15

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1550153 (SNAMPROGETTI) see Examples	1
X	GB 1440217 (ICI) see Examples	1
X	GB 1201014 (MERCK) see Examples and page 2 lines 27 to 38	1,5 & 8
X	GB 1072795 (EASTMAN KODAK) see Examples and page 1 lines 66 to 74	1,6,8
X	GB 833456 (ROHM & HAAS) see page 2 line 71	1
X	GB 768291 (SCHERING CORPORATION)	1
X	GB 766889 (W RAU) see page 1 line 69 to page 2 line 21	1
X	GB 708160 (PFIZER) see Examples	1
X	EP 0235986 A1 (ETHICAL GENERICS)	1,7
X	EP 0159602 A2 (ICI AUSTRALIA) see Examples	1,9
X	EP 0094513 A2 (AKZO GmbH) see Examples	1

Category	Identity of document and relevant passages	Relevant to claim 1)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&c Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

**Examiner's report to the Comptroller under
Section 17 (The Search Report)**

GB 9212430.4

Relevant Technical fields

(i) UK CI (Edition) Contd. from page 1

(ii) Int CI (Edition)

Databases (see over)

(i) UK Patent Office

(ii)

Search Examiner

J F JENKINS

Date of Search

30 SEPTEMBER 1992

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0017115 A2 (BASF) see Examples	1,2

SF2(p)

TP - doc99\fil000528

Category	Identity of document and relevant passages	Relevance to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

& Member of the same patent family, corresponding document.

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).